

Simple Digital Method for Resolving Overlapping Electronic Absorption Bands

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A new method of resolving overlapping electronic absorption bands is described. The method operates through linearizing Gaussian band shapes through derivation of $d \log \phi/d\nu$, where ϕ is the absorption band profile absorbance at wavelength ν . The simple, digital, method provides information of individual component peak positions, band heights (intensities), and widths. The limits of applicability for the method are given and extensions to include a visual display presentation are described. Results obtained using the method described are more consistent and accurate than results obtained using an analog curve resolver.

We are concerned with the problem of estimating the position, height, and width of absorption bands in experimentally obtained electronic absorption spectra. Various mathematical methods have been proposed for estimating peak parameters, but each method has its own advantages and disadvantages and no single procedure seems wholly adequate.

The two main types of methods are those which differentiate the spectra and those which rely on a least squares fitting procedure. The former methods include those described by Butler and Hopkins (1, 2) and by Morrey (3), while the latter methods are exemplified in the work of Tunnicliff and Wadsworth (4), Savitsky and Golay (5), and Schwartz (6). In these papers, the peak forms are usually assumed to be Gaussian, Lorentzian, or Student-T type envelopes. Siano and Metzler (7) have proposed a least-squares method based on a log-normal distribution.

The differentiation method is convenient but encounters difficulty if the order of differentiation is high, generally of second or fourth order, and if the spectrum includes noise. The least squares method is capable of great precision but usually depends upon initial estimates of the number of peaks and their parameters. A du Pont Curve Resolver is often necessary for preliminary analysis to obtain the initial peak parameters.

All the methods described require large digital computers for their application and, in most cases, the programs are written for equally-spaced data.

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- (1) W. L. Butler and D. W. Hopkins, *Photochem. Photobiol.*, **12**, 439 (1970).
- (2) W. L. Butler and D. W. Hopkins, *Photochem. Photobiol.*, **12**, 451 (1970).
- (3) J. R. Morrey, *Anal. Chem.*, **40**, 905 (1968).
- (4) D. D. Tunnicliff and P. A. Wadsworth, *Anal. Chem.*, **40**, 1826 (1968).
- (5) A. Savitsky and M. J. E. Golay, *Anal. Chem.*, **36**, 1627 (1964).
- (6) L. M. Schwarz, *Anal. Chem.*, **43**, 1336 (1971).
- (7) D. B. Siano and D. E. Metzler, *J. Chem. Phys.*, **51**, 1856 (1969).

THE METHOD

A spectral-resolution method is described that has the following properties: it assumes that the absorption peaks are Gaussian shaped as a function of wavenumber, ν ; it uses data taken at equal intervals in wavelengths, λ ; it permits filtering of the data to reduce noise without significant distortion; it provides reliable estimates of the peak positions, heights, and widths together with a criterion of accuracy; and it is not excessively long or complicated and is thus suitable for small computers, such as a Honeywell DDP 516 (8K core). It is assumed that the wavelength is perfectly known and the signal/noise ratio in absorbance is at least 200.

The method uses both least-squares fitting procedures and differentiation, and is probably closest in outlook to that of Tunnicliff and Wadsworth (4). The fundamental concept arises from the following considerations:

Suppose that the wavelength spectrum, $\phi(\nu)$, consists of a lone Gaussian peak centered at $\nu = A$, with height ϵ and width w , related to the standard deviation S by

$$w = 2S(2 \ln 2)^{1/2} \quad (1)$$

Then,

$$\phi(\nu) = \epsilon e^{-1/2 \left(\frac{\nu-A}{S} \right)^2} \quad (2)$$

and the quantity $\psi(\nu)$, defined by;

$$\psi(\nu) = d(-\ln \phi)/d\nu \quad (3)$$

satisfies

$$\psi(\nu) = (\nu - A)/S^2 \quad (4)$$

Hence, in a region where the wavenumber spectrum consists of a single Gaussian peak, the quantity $\psi(\nu)$ is linear in ν with Slope = $S^{-2} > 0$ and $\psi(0) = A$. When more than one peak is present in a spectrum, this will be true only in the regions where one peak dominates all of the other peaks.

Conceptually, the method proceeds as follows. The spectral data are submitted to the transformation Equation 3, the transformed data are plotted, and straight portions with positive slopes are sought. Each of these straight portions denotes a region where one peak dominates all the other peaks. Assuming that one such region can be found, the values of S and A are estimated from the plot and ϵ is estimated by using Equation 2,

$$\epsilon = \phi(\nu) e^{+\frac{1}{2} \left(\frac{\nu-A}{S} \right)^2} \quad (5)$$

With the parameters for that peak available, it is now possible to subtract it from the overall absorption envelope and then repeat the process for the next peak. In this way, the peaks are subtracted sequentially until they are all removed.

This procedure is quite straightforward to carry out when the data consist of spectral ordinates at equal increments in wavenumber ν . Normally one is concerned with the case where the spectral ordinates are available in equal increments of wavelength λ and, therefore, unequal increments in ν . The main problems in practical implementation are then: (i) to design a numerical differentiation procedure for Equation 3 that does not distort the peak shapes too much, and is also not excessively affected by the noise in the spectrum, and (ii) to develop a procedure for estimating A and S from the plot $\psi(\nu)$. Sometimes this can be done by simple graphical means, but it is desirable also to have an analytical method.

In treating problem (i) above, we shall adopt the criterion that our numerical process should be such as to minimize the distortion in a lone Gaussian peak. Naturally, this means that the regions where more than one peak contributes to the spectrum will be slightly distorted. This is not too serious a problem, however, because one can calculate peak parameters only from regions where one peak dominates.

If we define

$$\chi(\lambda) = \phi(\nu) \quad (6)$$

and use the relations

$$\lambda = \nu^{-1}, d\lambda/d\nu = -\nu^{-2} = -\lambda^2 \quad (7)$$

we obtain,

$$\psi(\nu) = \lambda^2 d(\ln \chi)/d\lambda \quad (8)$$

$$= d(\lambda^2 \ln \chi)/d\lambda - 2\lambda \ln \chi \quad (9)$$

If t is the constant wavelength increment between readings, we shall use the numerical differentiation formula,

$$d(\lambda^2 \ln \chi)/d\lambda = 1/(2t) \{(\lambda + t)^2 \ln \chi(\lambda + t) - (\lambda - t)^2 \ln \chi(\lambda - t)\}. \quad (10)$$

This formula is usually only an approximation, but, when applied to a lone Gaussian peak, it is exact because it is known to be exact for second degree polynomials, and $\lambda^2 \ln \chi$ is a second degree polynomial in λ ,

$$\lambda^2 \ln \chi = \lambda^2 \ln \epsilon - 1/2 \left(\frac{1 - A\lambda}{S} \right)^2 \quad (11)$$

Hence, we evaluate $\psi(\nu)$ by means of

$$\psi(\nu) = (2t)^{-1} \{ \eta(\lambda + t) - \eta(\lambda - t) \} - 2\lambda^{-1} \eta(\lambda) \quad (12)$$

$$\eta = \lambda^2 \ln \chi = \lambda^2 \ln \phi \quad (13)$$

and this formula is exact in regions where a single Gaussian peak dominates the spectrum.

To reduce the effect of noise on the differentiated spectrum, a three-point linear digital filter of the form,

$$\xi(\nu) = \left(\frac{1 - \gamma}{2} \right) \{ \eta(\lambda + t) + \eta(\lambda - t) \} + \gamma \eta(\lambda) \quad (14)$$

$$\psi(\nu) = 1/2t \{ \xi(\lambda + t) - \xi(\lambda - t) \} - 2\lambda^{-1} \eta(\lambda) \quad (15)$$

is used in place of Equation 12 if desired. γ is a constant which determines the filter properties; for $\gamma = 1$, Equation 15 reduces to Equation 12, and corresponds to no filtering at all. The best choice for noise suppression is $\gamma = 1/5$. Ap-

pendix I shows that the result of applying the filter to a lone Gaussian peak is Equation 4, i.e., the filter causes zero distortion of a lone Gaussian peak for any choice of γ .

Problem (ii) above is treated by a least-squares fitting procedure with orthogonal polynomials at equal intervals, see, e.g., Kendall and Stewart (8). For this purpose, the wavelengths at which the equally spaced measurements are taken are indexed as:

$$\lambda_j = \lambda_R + jt \quad j = 0, 1, 2, \dots \quad (16)$$

where λ_R is the initial wavelength. Then,

$$\nu_j = (\lambda_R + jt)^{-1} \quad (17)$$

and ν_j is not at equal increments. If j_0 be any one of the j -values, we set:

$$\lambda_0 = \lambda_R + j_0 t \quad (18)$$

and obtain:

$$\nu_j = \{ \lambda_0 + (j - j_0)t \}^{-1} \quad (19)$$

If $(j - j_0)t \ll \lambda_0$, we have approximately,

$$\nu_j = \lambda_0^{-1} - (j - j_0)t\lambda_0^{-2} \quad (20)$$

or

$$\nu_j = \nu_0 + (j - j_0)\delta_0 \quad (21)$$

where

$$\nu_0 = \lambda_0^{-1}, \text{ and } \delta_0 = -t\lambda_0^{-2} \quad (22)$$

From Equation 21, it can be seen that ν_j is spaced approximately equally for points near j_0 , the spacing being δ_0 . This will be sufficiently accurate in most cases, provided that $|j - j_0|$ is not too large. As j_0 changes, then both ν_0 and δ_0 change.

The slope and intercept (ν) of the transformed spectrum, $\psi(\nu)$, is estimated by fitting a second degree polynomial to each successive set of five ψ -ordinates, centered at j_0 . The method of least-squares (8) is applied to the data from the points with indices $j_0 - 2, j_0 - 1, j_0, j_0 + 1, j_0 + 2$, i.e., abscissas $\nu_0 - 2\delta_0, \nu_0 - \delta_0, \nu_0, \nu_0 + \delta_0, \nu_0 + 2\delta_0$. For that j_0 , estimates are obtained of the intercept, slope, curvature, and residual squared error. Estimated values of A and S are obtained from the slope and intercept, and ϵ is estimated from Equation 5 by averaging over the five data points. The process is repeated at each j_0 for which sufficient data are available. If this least-squares procedure is used, it may be unnecessary to initially filter the data, using Equation 14, since least-squares is itself a smoothing process. The filter is useful mostly when graphical methods are employed to estimate A and ν .

If ψ_j is assumed to have the behavior:

$$\psi_j = C_0 + C_1(\nu_j - \nu_0) + 1/2 C_2(\nu_j - \nu_0)^2 \quad (23)$$

near ν_0 , then we obtain estimates of the C 's from

$$C_2 = -2T_2/(7\delta_0^2) \quad (24)$$

$$C_1 = T_1/(10\delta_0) \quad (25)$$

and

$$C_0 = (T_0/5) + (2T_2/7) \quad (26)$$

where,

$$T_0 = \psi_{j_0-2} + \psi_{j_0-1} + \psi_{j_0} + \psi_{j_0+1} + \psi_{j_0+2} \quad (27)$$

$$T_1 = -2\psi_{j_0-2} + \psi_{j_0-1} + \psi_{j_0+1} + 2\psi_{j_0+2} \quad (28)$$

(8) M. G. Kendall and A. Stuart, "The Advanced Theory of Statistics," Vol. 2, Hafner, New York, N.Y., 1961, Chapter 28.

$$T_2 = -\psi_{j_0-2} + \frac{1}{2}\psi_{j_0-1} + \psi_{j_0} + \frac{1}{2}\psi_{j_0+1} - \psi_{j_0+2} \quad (29)$$

The sum of squared errors is:

$$E^2 = \sum_{m=-2}^2 [\psi(\nu_0 + m\delta_0)]^2 - (T_0^2/5) - (T_1^2/10) - (2T_2^2/7) \quad (30)$$

The estimated peak parameters are:

$$S = C_1^{-1/2} = (10\delta_0/T_1)^{1/2} \quad (31)$$

$$A = \nu_0 - (C_0/C_1) \quad (32)$$

and the curvature of the plot is C_2 . In general the curvature, e , will be negligible when

$$e = \frac{\frac{1}{2}|C_2|(2\delta_0)^2}{E} = \frac{2|C_2|\delta_0^2}{E} = \frac{4|T_2|}{7E} \ll 1$$

The presence of a portion of a single Gaussian peak is marked by nearly constant values of A , ϵ , and S over several adjacent values of j_0 and also by low values of e at the same points.

In general, it would be advantageous to remove the higher, wider peaks first. However, these peaks will have low values of ψ , and thus appear suppressed when compared with values of ψ from smaller, narrower peaks. The method will do badly if there is no region in which one peak dominates all of the others. Most methods experience difficulty for the case where no one peak dominates among others in a region. Thus, in differential methods, an illusion of a third peak arises when two peaks are resolved under certain conditions of relative height, width, and peak separation.

It is essential that any new proposed deconvolution methods be tested extensively such that the limits for accurate resolution of two overlapping absorption bands are delineated. All problems of band resolution reduce to the two band problem, and we thus frame the problem in general terms as that of resolving bands A and B, with positions ν_A and ν_B , intensities ϵ_A and ϵ_B and widths at half-height of w_A and w_B . The peak separation, $\nu_A - \nu_B$, is defined as Δ . Resolution of peaks A and B will be determined (in a general sense) by their relative size and the magnitude of Δ . Reduction of the six independent variables proceeds through expressing heights and widths as ratios, thus ϵ_A/ϵ_B and w_A/w_B . If ν_B , and ϵ_B and w_B are fixed and only ν_A , ϵ_A , and w_A varied, then the peak separation/band width properties are determined by the parameter w_A/Δ .

The criterion chosen for accurate resolution was that ν_A and ν_B must be at, or within, 1% of Δ from their actual positions. When the peak parameters are such that this condition is obeyed, the resolution is considered successful. In Figure 1, the limits of conditions for the successful resolution are plotted as a function of w_A/w_B vs. w_A/Δ for given ϵ_A/ϵ_B ratios.

The cusp behavior in the region of $w_A/w_B = 1.7$, $w_A/\Delta = 0.6$ for $\epsilon_A/\epsilon_B = 1.0$, occurs when the two peaks overlap such that one peak does not dominate the other completely. When one peak is much larger than the second, and Δ is relatively small, ψ for the first peak provides a background upon which the contribution from ψ for the second may be recognized. The other extreme, i.e., at large Δ , shows ψ 's from each peak separately and clearly. The cusp condition arises where the "tail" of the first, larger, peak interferes only partially with the second peak.

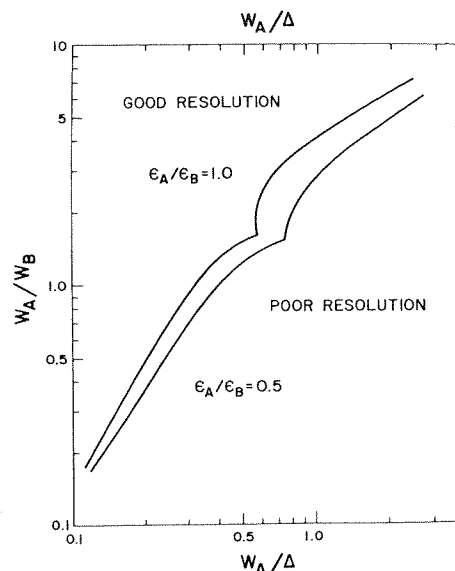


Figure 1. Presentation of the limits of resolution by this method plotted on a logarithmic scale as a function of w_A/w_B vs. w_A/Δ for various ϵ_A/ϵ_B ratios

In the region of good resolution, the method successfully resolves two bands to give both values of ν_{\max} accurate to less than 1% of Δ . In the region of poor resolution, the method gives progressively more inaccurate values for the band maxima as w_A/Δ increases

APPLICATIONS OF THE COMPUTER PROGRAM

The program of the method described above presents the original absorption profile when called as the appropriate data set number from a backing disc store. The data may be filtered if required, preferably for a graphical analysis only. The program then transforms the data using Equations 14 and 15 and carries out the least mean squares fitting at each j_0 .

Output may take two forms. The first form is a table of λ , ν , ϕ , ψ , A , ϵ , S , and e in which peaks are recognized by constant values of A , E , and S and low values of e .

The second form of output gives the original absorption profile, ϕ , and ψ , the first derivative of $\log \phi$, on a graph plotter from which linear portions of ψ may be recognized. Feedback of the limits of the linear portions of ψ into the program will remove the associated peaks. In practice, several attempts are required to optimize peak removal and plotting each set of graphs requires considerable time.

The alternative version of the graphical output presents the graphs in sequence on a Tektronix 4002A Visual Display Unit, with a joystick control. In this mode, several attempts may be made to remove peaks within a short time and only the optimum peak removal (identification) plotted to give a hard copy.

As an example, the absorption spectrum of iodide dissolved in a range of solvents in the far-ultraviolet region shows a series of overlapping bands (9). The example given in Figure 2, is that of tetra-*n*-butyl ammonium iodide in triethyl phosphate at 253 K (10). The original spectrum is displayed in Figure 2A as ϕ , with normalization 2×10^2 . Figure 2B shows $d \log A/d\nu$ plotted vs. ν , i.e., ψ , with an initial linear region encompassed by the crosswire marks. It is advantageous to look at the linear portion selected, and Figure 2C shows the section of ψ which was chosen expanded to full scale. Further selections of ψ may be attempted

(9) M. F. Fox and E. Hayon, *Chem. Phys. Lett.*, **14**, 442 (1972).

(10) M. F. Fox and E. Hayon, to be published.

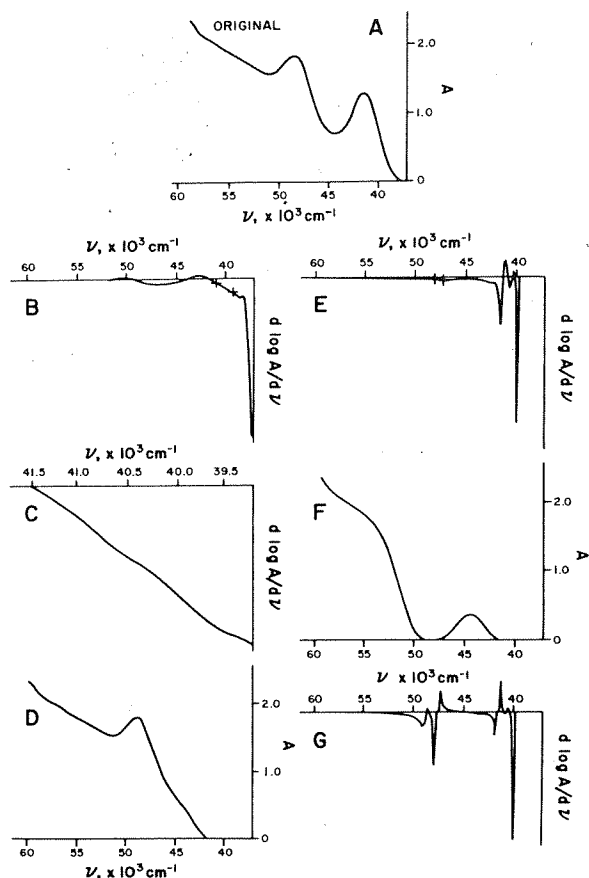


Figure 2. Visual data display for 5×10^{-3} tetra-*n*-butylammonium iodide in triethyl phosphate at 253 K

(A) Experimentally obtained absorption spectra, ϕ . (B) $d \log A/d\nu$ of (A) plotted vs. ν , (ψ), showing crosswires controlled by joystick. (C) Expansion of ψ between the crosswires of (B) above showing region of interest for peak removal. (D) ϕ , i.e., (A) with the first peak removed. This spectrum is then made an original data, as ϕ' . (E) $d \log A/d\nu$, (ψ') of (D) showing linear region denoted by crosswires. (F) (A) with second peak removed. The remaining data are then treated as an original data set, ϕ'' . (G) $d \log A/d\nu$ for (F) giving the band parameter of the small band at approx. $44,000 \text{ cm}^{-1}$

until a decision to remove the band associated with that linear portion is made. The spectrum ϕ , after optimal removal of the first band, Figure 2D, contains, among others, a hitherto unsuspected low intensity band. The initial spectrum, ϕ ; and the residual spectrum after the first band has been removed, ϕ' , may then be plotted to give a hard copy.

The residual spectrum ϕ' , is then reprocessed to give ψ' wherein a further linear portion, delineated by the crosswire marks, is noted as in Figure 2E. Optional removal of the second large band gives the second residual spectrum, ϕ'' in Figure 2F showing the previously described small band in isolation. The parameters of the small band in the region of $44,000 \text{ cm}^{-1}$ may be obtained by further processing of ϕ'' to obtain ψ'' , Figure 2G. Attempts to remove further bands are not successful because the individual components are too overlapped for accurate deconvolution, the "poor resolution" condition of Figure 1 applying. Further band resolution can only be achieved using an analog curve resolver on a subjective basis, using as few bands as is consistent with an acceptable solution.

Comparison with other methods shows the method described here to give more consistent results for a set of spectra recorded over a range of temperature than obtained using the analog curve resolver approach. The advantages of the digital method being that one peak, and thus a small

part of an overall absorption profile, is dealt with at each treatment and the parameters are obtained from a least mean squares approach.

Such considerations are the more advantageous when it is realized that a spectral width of $25,000 \text{ cm}^{-1}$ is presented on the ten-inch scale of the analog resolver.

On the other hand, the method is not as effective as the iterative least mean squares method of fitting a series of Gaussian (normal) or log-normal curves to an absorption profile. The advantages of the iterative method lie with the absence of differential operators and the small but very effective adjustments which are made to obtain an accurate solution.

A program listing, with worked examples, is available upon request from the authors.

APPENDIX I: DERIVATION OF THE FILTER EQUATIONS

In this Appendix, we shall show that the filter defined by Equations 14 and 15 leads to Formula 4 when applied to a lone Gaussian peak.

For such a peak, Equations 11 and 13 imply

$$\eta_\lambda = \eta(\lambda) = \lambda^2 \ln \epsilon - \frac{1}{2} \left(\frac{1 - A\lambda}{S} \right)^2 \quad (\text{I.1})$$

We assume that the filter has the three-point, linear, digital form

$$\zeta_\lambda = \gamma_{-1}\eta_{\lambda-1} + \gamma\eta_\lambda + \gamma_1\eta_{\lambda+1} \quad (\text{I.2})$$

where

$$\left. \begin{aligned} \zeta_{\lambda+m} &\equiv \zeta(\lambda + mt) \\ \eta_{\lambda+m} &\equiv \eta(\lambda + mt) \end{aligned} \right\} \quad m = \dots -2, -1, 0, 1, 2, \dots \quad (\text{I.3})$$

and γ_{-1} , γ , γ_1 are constants to be specified later. If we substitute the form of η_λ , Equation I.1, into I.2, use I.3 and collect terms, we obtain after some algebra

$$\zeta_\lambda = (\lambda^2\sigma + 2\theta_0\lambda t + \sigma_0 t^2) \ln \epsilon - \frac{1}{2S^2} [\sigma(1 - A\lambda)^2 - 2At\theta_0(1 - A\lambda) + A^2 t^2 j_0] \quad (\text{I.4})$$

where

$$\sigma \equiv \gamma_{-1} + \gamma + \gamma_1$$

$$\sigma_0 \equiv \gamma_{-1} + \gamma_{-1}$$

$$\theta_0 \equiv \gamma_{-1} - \gamma_{-1}$$

Using Equation I.4, we obtain after some more algebra

$$\frac{1}{2t} [\zeta_{\lambda+1} - \zeta_{\lambda-1}] = 2(\lambda\sigma + \theta_0 t) \ln \epsilon - \frac{A}{S^2} [-\sigma + A(\lambda\sigma + \theta_0 t)] \quad (\text{I.5})$$

Equations 2, 6, and 7 lead to

$$\ln \chi(\lambda) = \ln \chi_\lambda = \ln \epsilon - \frac{1}{2} \left(\frac{\lambda^{-1} - A}{S} \right)^2$$

or

$$2(\lambda\sigma + \theta_0 t) \ln \chi_\lambda = 2(\lambda\sigma + \theta_0 t) \ln \epsilon - \frac{(\lambda\sigma + \theta_0 t)}{S^2} (\lambda^{-2} - 2A\lambda^{-1} + A^2) \quad (\text{I.6})$$

Subtracting Equation I.6 from I.5 and simplifying the result, we find

$$Q_{\lambda} \equiv \frac{1}{2t} [\zeta_{\lambda+1} - \zeta_{\lambda-1}] - 2(\lambda\sigma + \theta_0 t) \ln \chi_{\lambda} = \frac{1}{S^2} [\sigma(\lambda^{-1} - A) + \theta_0 t \lambda^{-1}(\lambda^{-1} - 2A)] \quad (\text{I.7})$$

We have not yet chosen the filter constants γ_{-1} , γ , and γ_1 . We now choose them so that the final form of the filter, given by Q_{γ} , leads to Equation 4. Equation I.7 tells us that we can do that only by choosing

$$\theta_0 = 0 \quad \text{and} \quad \sigma = 1$$

or

$$\gamma_1 = \gamma_{-1} = (1 - \gamma)/2 \quad (\text{I.8})$$

With this choice we obtain

$$Q_{\lambda} \equiv \frac{1}{2t} [\zeta_{\lambda+1} - \zeta_{\lambda-1}] - 2\lambda^{-1}\eta_{\lambda} = \frac{\lambda^{-1} - A}{S^2}$$

or from Equations 7 and 13

$$Q_{\lambda} \equiv \frac{1}{2t} [\zeta_{\lambda+1} - \zeta_{\lambda-1}] - 2\lambda^{-1}\eta_{\lambda} = \frac{\nu - A}{S^2} \quad (\text{I.9})$$

Also, combining Equations I.8 and I.2, we find that

$$\zeta_{\lambda} \equiv \zeta(\lambda) = \left(\frac{1 - \gamma}{2} \right) [\eta(\lambda - t) + \eta(\lambda + t)] + \gamma\eta(\lambda) \quad (\text{I.10})$$

Equation I.10 is the same as Equation 14.

We see from Equations I.9 and I.2 that the quantity

$$Q_{\lambda} \equiv \frac{1}{2t} [\zeta(\lambda + t) - \zeta(\lambda - t)] - 2\lambda^{-1}\eta(\lambda) \quad (\text{I.11})$$

where $\zeta(\lambda + t)$ and $\zeta(\lambda - t)$ are defined by Equation I.10, gives the number $(\nu - A)/S^2$ when applied to a lone Gaussian peak with parameters A and S . This means that we may interpret Q_{λ} as the filtered version of $\psi(\nu)$; that is, we may take Q_{λ} to be the definition of $\psi(\nu)$ when the data are subjected to a three-point, linear digital filter of the form of Equation I.10. This leads to Equation 15.

Notice that the filter gives the correct values for $\psi(\nu)$,

namely $(\nu - A)/S^2$, regardless of the choice of the constant γ . The value of γ determines the properties of the filter. If $\gamma = 1$, we obtain

$$\zeta(\lambda) = \eta(\lambda)$$

$$\psi(\nu) = \frac{1}{2\Delta} \{ \eta(\lambda + t) - \eta(\lambda - t) \} - 2\lambda^{-1}\eta(\lambda)$$

For this choice of γ , the filter gives the same result, Equation 12, that is obtained when there is no filter. If the noise is low-level, uncorrelated, and Gaussian, and if the peak is sufficiently wide compared to the spacing, it can be shown that $\gamma \approx 1/5$ gives the least variance in the filter output. However, filtering can cause originally uncorrelated noise to become correlated and can also cause loss of resolution, so it may be preferable to use a γ -value nearer to unity.

The filter (I.10) can be repeated N times according to the formula

$$\zeta^{(n)}(\lambda) = \frac{1 - \gamma}{2} [\zeta^{(n-1)}(\lambda - t) + \zeta^{(n-1)}(\lambda + t)] + \gamma\zeta^{(n-1)}(\lambda) \quad \text{for } n = 1, 2, \dots, N \quad (\text{I.12})$$

$$\zeta^{(0)}(\lambda) = \eta(\lambda) \quad (\text{I.13})$$

If $\zeta^{(N)}(\lambda)$ is substituted into

$$\psi(\nu) = Q_{\lambda} = \frac{1}{2t} [\zeta^{(N)}(\lambda + t) - \zeta^{(N)}(\lambda - t)] - 2\lambda^{-1}\eta(\lambda) \quad (\text{I.14})$$

the result is again $(\nu - A)/S^2$ for a lone Gaussian peak. That is, filtering N times according to Equations I.12 and I.13, then substituting the final results, $\zeta^{(N)}(\lambda)$, into Equation I.14 causes no distortion of a pure Gaussian peak. Filtering several times can reduce the noise into a lower level than filtering only once. However, it is risky to filter too many times because of resolution loss.

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